

# A New Cd(II) Coordination Compound Based on 4-(1,2,4-Triazol-4-yl)phenylacetic Acid: Synthesis, Structure and Photoluminescence Property

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**ABSTRACT** A new complex  $[\text{Cd}_2(\text{L})_2(\text{Cl})_2(\text{H}_2\text{O})]_n$  (**1**) was synthesized by reacting  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  with 4-(1,2,4-triazol-4-yl)phenylacetic acid (HL) ligand. The structure of the complex was characterized by single-crystal X-ray diffraction, IR spectroscopy, elemental analysis and PXRD. Complex **1** crystallizes in triclinic, space group  $P2_1/c$  with  $a = 11.4303(8)$ ,  $b = 14.1792(10)$ ,  $c = 14.6857(10)$  Å,  $\beta = 96.3780(10)^\circ$ ,  $V = 2365.4(3)$  Å<sup>3</sup>,  $Z = 4$ ,  $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{N}_6\text{O}_5\text{Cd}_2$ ,  $M_r = 716.09$ ,  $D_c = 2.011$  g/cm<sup>3</sup>,  $\mu = 2.069^{-1}$ ,  $S = 1.051$ ,  $F(000) = 1392$ , the final  $R = 0.0458$  and  $wR = 0.0949$  for 5402 observed reflections ( $I > 2\sigma(I)$ ). Complex **1** is a two-dimensional (2D) layer structure and non-covalent bonding interactions such as  $\text{C-H} \cdots \pi$  and  $\pi \cdots \pi$  extend the 2D to form a three-dimensional supramolecular polymer.

**Keywords:** synthesis; supramolecular polymer; photoluminescent property;

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## 1 INTRODUCTION

The rational design and fabrication of metal-organic frameworks (MOFs) have flourished as an emerging area of research because of their promising applications in guest molecule inclusion, gas and vapor storage, chemical sensing, magnetism, heterogeneous catalysis, etc<sup>[1-5]</sup>. Although synthetic conditions have great influence on the structures of the resulted complexes such as reaction temperature, solvent, pH of the medium, ligand-to-metal ratios and choice of metal precursors, the most important factor for the construction of desired MOFs is the judicious choice of appropriate linkers<sup>[6, 7]</sup>. In addition, the typical non-covalent interactions (such as H-bonding and  $\pi/\pi$  stacking  $\text{C-H} \cdots \pi$ )<sup>[8-10]</sup> also play important roles in the assembly of supramolecular polymers. As for ligands linkers, the N- and/or O-donors have been extensively to build novel MOFs with interesting structures and properties<sup>[11, 12]</sup>. Among the N-donors, the imidazole, triazole and tetrazole analogues are widely employed in the construction of MOFs. Our groups have engaged in the design of N-donor

4-imidazole ligands, such as 1,4-di(1H-imidazol-4-yl)benzene and 1,3,5-tri(1H-imidazol-4-yl)benzene, which exhibit diverse coordination modes<sup>[13-15]</sup>. Furthermore, we have constructed diverse frameworks with favorable gas adsorption or selective gas adsorption properties based on the metal-imidazolate units. Similarly, the O-donors of carboxylate groups have versatile coordination modes as well, and thus the designable ligands incorporating multi-N and carboxylate groups may be a useful strategy for the construction of novel MOFs<sup>[16, 17]</sup>. Therefore, our groups have furthermore designed difunctional organic linker combining carboxyl and 4-imidazolyl donors such as 4-(1H-imidazol-4-yl)benzoic acid which are employed as good candidates for the construction of MOFs in our previous study<sup>[18]</sup>. Taking favorable coordination ability of the multi-N and O-donor into account, we synthesized the ligand of 4-(1,2,4-triazol-4-yl)phenylacetic acid (HL) containing the triazolyl and carboxyl groups, which may exhibit rich coordination modes in the assembly of MOFs. Herein, we report the synthesis and crystal structure of a new coordination polymer  $[\text{Cd}_2(\text{L})_2(\text{Cl})_2(\text{H}_2\text{O})]_n$  (**1**) obtained by the reaction of HL and  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  as an extension of our previous work.

## 2 EXPERIMENTAL

### 2.1 Materials and measurements

All the commercially available chemicals and solvents were of reagent grade and used as received without further purification. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer using KBr pellets. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT 2960 thermal analyzer under nitrogen at a heating rate of 10 °C/min. Power X-ray diffraction (PXRD) patterns were measured on a Shimadzu XRD-6000 X-ray diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation at room temperature.

### 2.2 Synthesis of complex $[\text{Cd}_2(\text{L})_2(\text{Cl})_2(\text{H}_2\text{O})]_n$ (**1**)

A mixture of HL (0.020 g, 0.1 mmol),  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.022 g, 0.1 mmol) and 10 mL  $\text{H}_2\text{O}$  was adjusted to  $\text{pH} = 7$  with 0.5 mol  $\text{L}^{-1}$  solution. The mixture was then sealed into a 20 mL Teflon-lined stainless-steel container and heated at 160 °C for 48 h. Colorless block crystals of **1** were collected with a yield of 42% by filtration and washed with water and ethanol for several times. Anal. Calcd. (%) for  $\text{C}_{20}\text{H}_{16}\text{Cl}_2\text{N}_6\text{O}_5\text{Cd}_2$ : C, 33.54; H, 2.25; N, 11.74. Found (%): C, 33.33; H, 2.41; N, 11.61. IR(KBr): 3215 (w), 1591 (s), 1575 (vs), 1543 (m), 1529 (vs), 1395 (vs), 1243 (m), 1093 (s), 1037 (m), 1019 (m), 821 (m), 777 (s), 670 (w), 638 (w), 588 (w), 515 (w)  $\text{cm}^{-1}$ .

## 2.3 Crystal structure determination

The colorless crystals of complex **1** were selected for diffraction data collection at 296(2) K on a Bruker Smart Apex II CCD diffractometer equipped with a graphite-monochromatic Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). A total of 14109 reflections were collected for **1**, of which 5402 ( $R_{\text{int}} = 0.0574$ ) were independent in the range of  $1.79 \leq \theta \leq 27.62^\circ$  by using a  $\varphi$ - $\omega$  scan mode. The structure was solved by direct methods with SHELXS-97<sup>[19]</sup> program and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-97<sup>[20]</sup>. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in their calculated positions and refined following the riding model. The final  $R = 0.0458$ ,  $wR = 0.0949$  ( $w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.4516P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ ),  $R_{\text{int}} = 0.0574$ ,  $(\Delta/\sigma)_{\text{max}} = 0.000$ ,  $S = 1.051$ ,  $(\Delta\rho)_{\text{max}} = 1.230$  and  $(\Delta\rho)_{\text{min}} = -1.193$  e/Å<sup>3</sup> for **1**. The selected bond distances and bond angles for complex **1** are listed in Tables 1 and 3, respectively.

## 3 RESULTS AND DISCUSSION

### 3.1 Crystal structure of **1**

Single-crystal X-ray diffraction analysis revealed that complex **1** crystallizes in the monoclinic system with space group  $P2_1/c$ . The asymmetric unit of **1** contains two crystallographically independent Cd(II) atoms, two Cl<sup>−</sup> anions, two L<sup>−</sup> ligands and one coordinated water molecule. As exhibited in Fig. 1, the Cd(1) atom has octahedral coordination geometry with N<sub>2</sub>O<sub>3</sub>Cl binding set coordinated by two nitrogen (N(1), N(4)) atoms from two L<sup>−</sup> ligands, two oxygen atoms (O(1D), O(4B) and O(7)) from other two L<sup>−</sup> ligands, one oxygen (O(7)) from coordinated water molecule and one Cl<sup>−</sup> anion, while Cd(2) is also octahedral coordination geometry with NO<sub>3</sub>Cl<sub>2</sub> coordination sphere. The Cd–O distances are in the range of 2.229(5)~2.420(4)(19) Å while the Cd–N distances are 2.316(5) 2.382(5) Å, and the coordination angles around Cd(II) are in the range of 73.27(6)~180.0° (Table 1). A notable feature of the structure of **1** is that the HL ligands exhibit two coordination modes existing together in one compound (Fig. 2): (i) one acts as a  $\mu_3$ -bridging linker, using one N atom to bridge one Cd(II) atom and two oxygen atoms from carboxyl group in the  $\mu_2$ - $\eta^1$ : $\eta^1$ -bridging mode to ligate two Cd(II) atoms; (ii) the other one adopts  $\mu_4$ -bridging modes, using two N atoms to bridge two Cd(II) atoms and the carboxyl group in  $\mu_3$ - $\eta^2$ : $\eta^1$ -bridging mode to chelate two Cd(II) atoms. Two adjacent Cd(II) ions are alternately linked together by one triazolate group, one carboxylate group, and one bridged Cl<sup>−</sup> ion with the distances of 3.994(7) and 4.056(7) Å to give a one-dimensional (1D) chain (Fig. 3). It is noteworthy that both

of two different  $L^-$  ligands connect Cd(II) atoms to form 1D chains respectively, and these two 1D chains intersect each other, forming a 1D helix chain structure (Fig. 4a). Similarly, there are two different  $Cl^-$  anions, one acting as a terminal coordination atom to balance the positive charges while another employing as  $\mu_2$ -bridging to connect the Cd(II) atom. Because of the bridging interaction of triazole and carboxyl group together with  $Cl^-$ , the 1D chains are further connected into a two-dimensional (2D) layer structure (Fig. 4b). And the hydrogen bonding interactions ( $C(1) \cdots Cl(2)$  3.56 Å,  $C(1)-H(1) \cdots Cl(2)$  148°,  $C(5) \cdots N(5)^a$  3.48 Å,  $C(5)-H(5) \cdots N(5)$  160°,  $O(2) \cdots O(7)$  3.36 Å,  $O(2)-H(5) \cdots O(7)$  156°,  $C(8) \cdots Cl(2)$  3.55 Å,  $C(8)-H(8) \cdots Cl(2)$  165°) exist in the 2D structure (Table 2), further reinforcing the stability of this complex. For the overall framework of **1**, it can be seen clearly that the 2D layers repeat in the unit  $\cdots AAA \cdots$  stacking sequence along the  $b$  axis, and numerous intramolecular  $\pi$ - $\pi$  and C-H  $\cdots \pi$  interactions exist among the aromatic rings, as shown in Fig. 5. The benzene rings of the  $L^-$  ligands between the adjacent 2D layers are parallel and are separated by a centroid-centroid distance of 3.68 Å and C-H  $\cdots \pi$  distance of 2.96 Å<sup>[21, 22]</sup>. The non-classic weak  $\pi$ - $\pi$  and C-H  $\cdots \pi$  interactions further link the 2D layers into a three-dimensional (3D) supramolecular polymer (Fig. 5).

### 3.2 IR spectrum, thermal stabilities and powder X-ray diffraction of **1**

The infrared spectrum of the complex has been recorded between 4000 and 450  $cm^{-1}$  and some important assignments are shown in the experimental section (Fig. 6). Strong characteristic bands of carboxylic group are observed in the range of 1590~1529  $cm^{-1}$  for asymmetric vibrations. The carboxylic acid of HL is deprotonated to form  $L^-$  ligand, and the strong absorption band around 1590  $cm^{-1}$  is attributed to the asymmetric stretching vibration of C=O group, which is significantly smaller than that of the protonated carboxylate group monomer (1695  $cm^{-1}$ ), indicating the delocalization of C=O double bond<sup>[23]</sup>. Complex **1** was subjected to thermogravimetric analysis (TGA) to ascertain the stability of supramolecular architecture, and the result is shown in Fig. 7. A total weight loss of 2.36% was observed for **1** around 90 °C, which is attributed to the loss of coordinated water molecule (calcd. 2.51%), and the residue is stable up to about 380 °C. Powder XRD experiment was carried out to confirm the phase purity of bulk sample (Fig. 8), and the experimental pattern of the as-synthesized sample is comparable to the corresponding simulated one, indicating the phase purity of the sample.

### 3.3 Photoluminescent property

It is known that coordination polymers with  $d^{10}$  closed-shell metal center with the rational selection and design of conjugated organic spacers may exhibit excellent fluorescence properties and serve as good candidates for potential applications as photoactive materials<sup>[24, 25]</sup>. We investigate the solid-state fluorescence property of complex **1** as well as the HL<sub>1</sub> ligand at room temperature. The free HL<sub>1</sub> ligand shows intense emission band at 440 nm upon excitation at 365 nm, which may be attributed to  $\pi^* \rightarrow \pi$  transition of the intraligands<sup>[26, 27]</sup>, while complex **1** exhibits light blue emission with maximum at 433 nm upon excitation at 355 nm as depicted in Fig. 9. By contrast with the free ligand, the emission bands of complex **1** are 7 nm blue-shifted. Such broad emission bands may be tentatively assigned to ligand-to-metal charge transfer (LMCT)<sup>[28, 29]</sup>. In addition, Fig. 9 shows that the luminescence intensity of **1** has increased compared with the free ligand under the same conditions, which may mainly originate from the coordination interactions between the metal Cd(II) atom and the ligand, thus enhancing its conformational rigidity and then decreasing the non-radiative energy loss<sup>[30]</sup>. Therefore, complex **1** may appear to be potential hybrid inorganic-organic photoactive material.

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**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of  $[Cd_2(L)_2(Cl)_2(H_2O)]_n$**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–N(4)	2.315(5)	Cd(1)–O(4)#B	2.228(5)	Cd(1)–O(7)	2.329(4)
Cd(1)–O(1)#D	2.340(4)	Cd(1)–N(1)	2.361(5)	Cd(1)–Cl(1)	2.5292(18)

Cd(2)–O(3)#B	2.344(4)	Cd(2)–N(2)#C	2.381(5)	Cd(2)–O(2)#A	2.401(4)
Cd(2)–O(1)#A	2.421(4)	Cd(2)–Cl(2)	2.4788(17)	Cd(2)–Cl(1)	2.4896(18)
Angle	(°)	Angle	(°)	Angle	(°)
O(4)#B–Cd(1)–N(4)	92.3(2)	O(4)#B–Cd(1)–O(7)	170.44(18)	N(4)–Cd(1)–O(7)	82.15(19)
O(4)#B–Cd(1)–O(1)#D	89.63(17)	N(4)–Cd(1)–O(1)#D	82.43(17)	O(7)–Cd(1)–O(1)#D	81.96(15)
O(4)#B–Cd(1)–N(1)	97.66(19)	N(4)–Cd(1)–N(1)	157.11(18)	O(7)–Cd(1)–N(1)	84.94(17)
O(1)#D–Cd(1)–N(1)	77.10(15)	O(4)#B–Cd(1)–Cl(1)	100.90(14)	N(4)–Cd(1)–Cl(1)	100.15(15)
O(7)–Cd(1)–Cl(1)	87.78(12)	O(1)#D–Cd(1)–Cl(1)	169.00(11)	N(1)–Cd(1)–Cl(1)	98.14(13)
O(3)#B–Cd(2)–N(2)#C	79.85(18)	O(3)#B–Cd(2)–O(2)#A	168.89(16)	N(2)#C–Cd(2)–O(2)#A	93.13(17)
O(3)#B–Cd(2)–O(1)#A	116.08(16)	N(2)#C–Cd(2)–O(1)#A	76.03(15)	O(2)#A–Cd(2)–O(1)#A	53.39(14)
O(3)#B–Cd(2)–Cl(2)	88.72(12)	N(2)#C–Cd(2)–Cl(2)	151.19(13)	O(2)#A–Cd(2)–Cl(2)	93.56(12)
O(1)#A–Cd(2)–Cl(2)	85.70(10)	O(3)#B–Cd(2)–Cl(1)	96.06(12)	N(2)#C–Cd(2)–Cl(1)	91.61(13)
O(2)#A–Cd(2)–Cl(1)	92.70(11)	O(1)#A–Cd(2)–Cl(1)	142.16(11)	Cl(2)–Cd(2)–Cl(1)	116.00(7)

Symmetry transformation: A:  $-1-x, -0.5+y, 1.5-z$ ; B:  $1-x, -0.5+y, 1.5-z$ ; C:  $-x, -0.5+y, 1.5-z$ ; D:  $1+x, y, z$

Table 2. Hydrogen Bonding Interactions for Complex 1 (Å, °)

D–H ⋯ A	D–H	H ⋯ A	D ⋯ A	∠DHA
C(1)–H(1) ⋯ Cl(2)	0.93	2.74	3.560(8)	148
C(5)–H(5) ⋯ N(5) <sup>a</sup>	0.93	2.59	3.478(9)	160
C(8)–H(8) ⋯ Cl(2)	0.93	2.64	3.550(7)	165

Symmetry code: (a)  $-x, 0.5+y, 1.5-z$

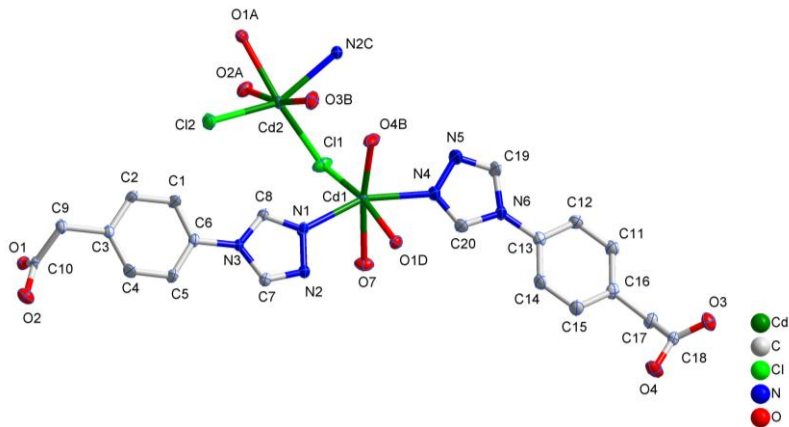


Fig. 1. Coordination environment of Mn(II) in complex 1 with ellipsoids drawn at 30% probability level. Hydrogen atoms were omitted for clarity (Symmetry codes: (A)  $-1-x, -0.5+y, 1.5-z$ ; (B)  $1-x, -0.5+y, 1.5-z$ ; (C)  $-x, -0.5+y, 1.5-z$ ; (D)  $1+x, y, z$ )



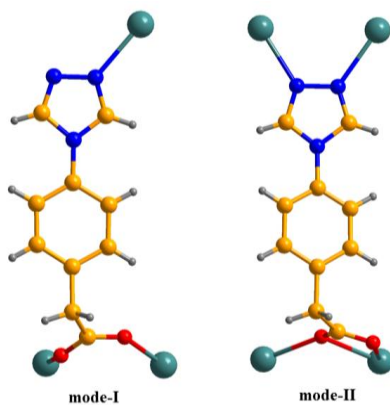


Fig. 2. Coordination environment of 4-tba ligands in complex 1

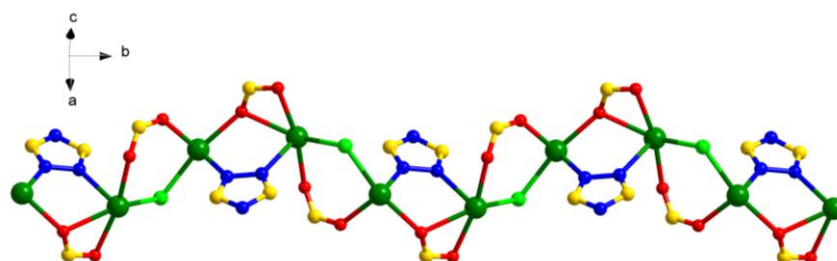


Fig. 3.  $\text{Cl}^-$  and carboxyl group-bridged 1D  $\text{Cd}(\text{II})$  chains for 1

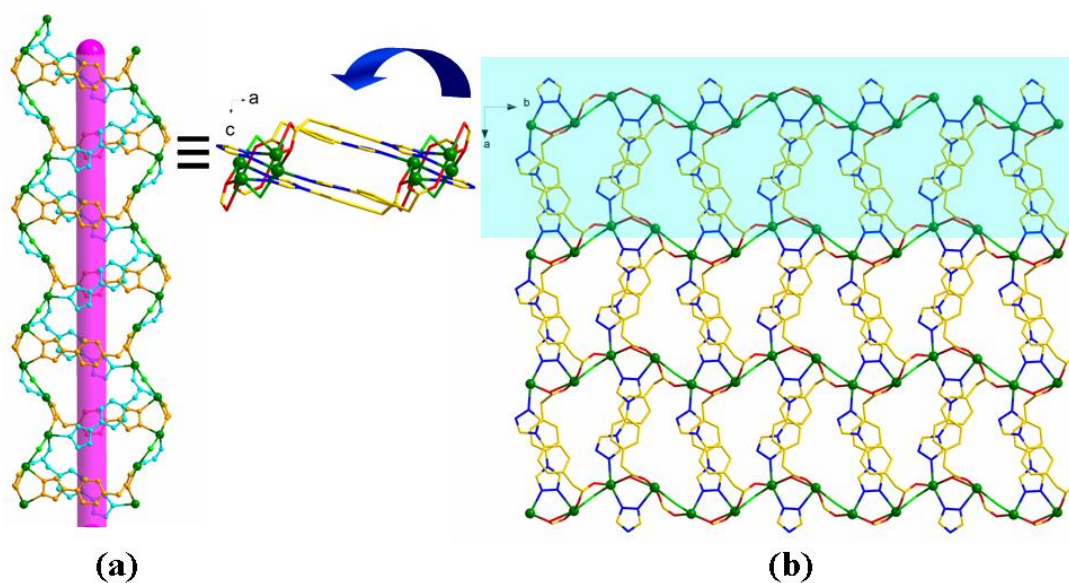


Fig. 4. 1D chain (a) and 2D network (b) of 1



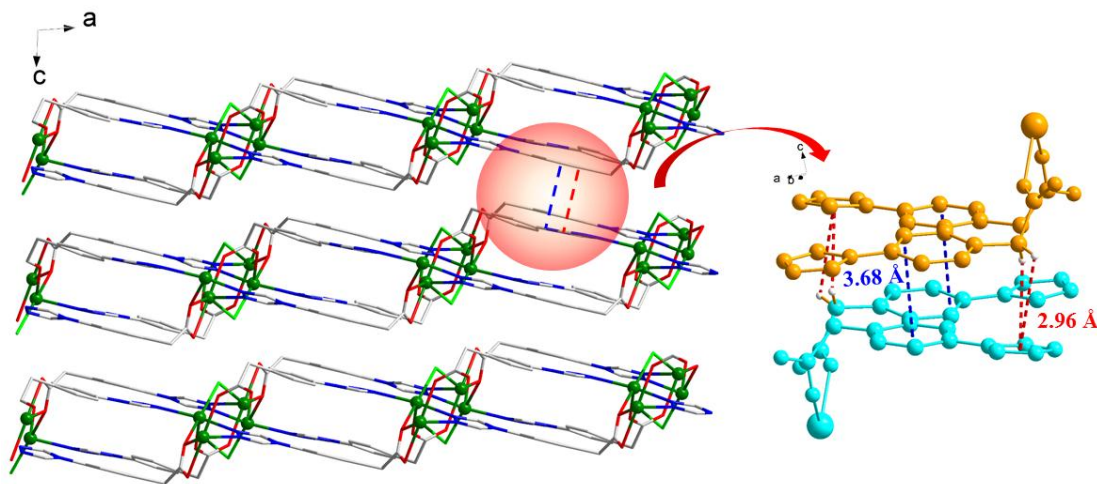


Fig. 5. 3D supramolecular structure constructed from 2D stacking units in sequence of AAA along the *b* axis, linked by  $\pi \cdots \pi$  and C-H  $\cdots \pi$  stacking interactions

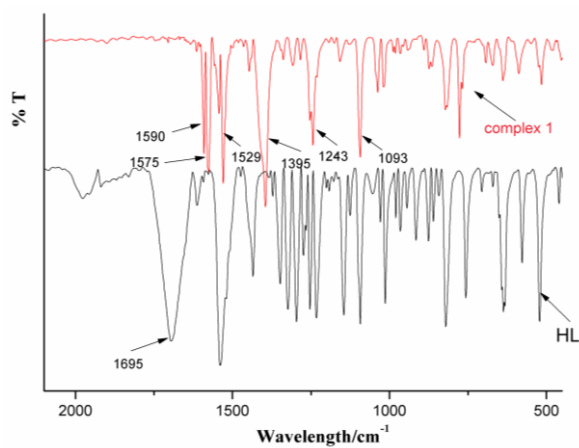


Fig. 6. IR spectra of HL and complex 1

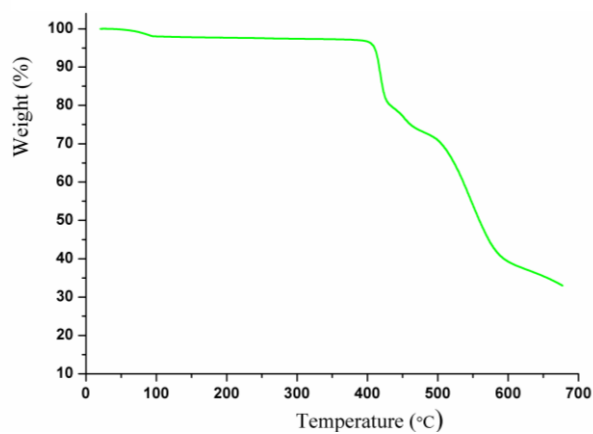


Fig. 7. TG curves of complex 1

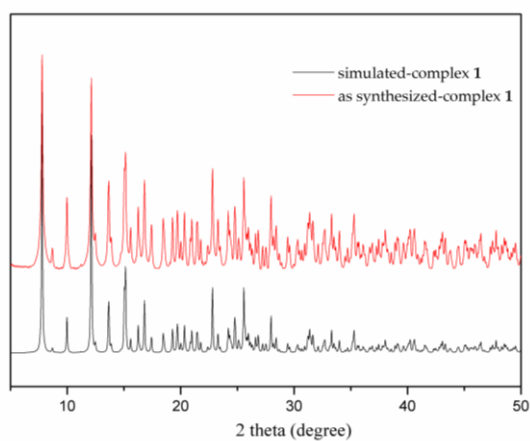
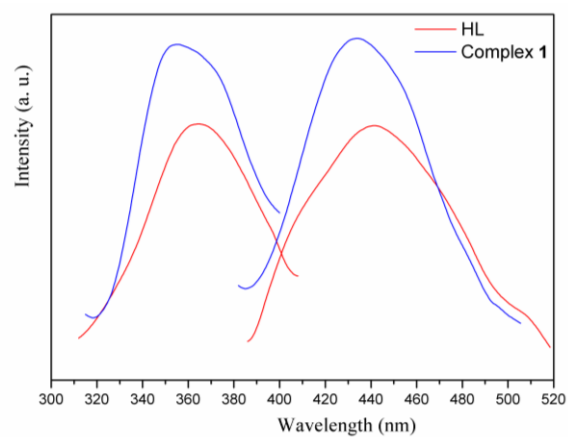


Fig. 8. Simulated and experimental XRPD patterns of complex 1



**Fig. 9.** Solid-state photoluminescent spectra of HL and complex 1 at room temperature

**A New Cd(II) Coordination Compound**  
**Based on 4-(1,2,4-Triazol-4-yl)phenylacetic Acid:**  
**Synthesis, Structure and Photoluminescence Property**

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XIAO Li(肖丽) CHEN Shui-Sheng(陈水生)

A new complex of  $[\text{Cd}_2(\text{L})_2(\text{Cl})_2(\text{H}_2\text{O})]_n$  (**1**) based on 4-(1,2,4-triazol-4-yl)phenylacetic acid containing triazolyl and carboxyl difunctional groups has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction. Complex **1** is a two-dimensional layer structure and non-covalent bonding interactions such as  $\text{C-H} \cdots \pi$  and  $\pi \cdots \pi$  extend the 2D to form a three-dimensional supramolecular polymer.

